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# COLLOIDS AND FLOTATION

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BY

FREDERICK G. MOSES

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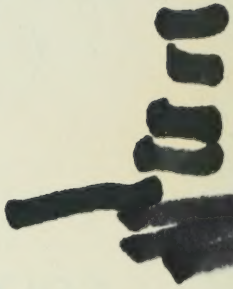

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# COLLOIDS AND FLOTATION.

By Frederick G. Moses.

## INTRODUCTION.

The development of the flotation process during the past five years has been rapid. Practical knowledge of the process has increased at nearly the same rate. Many details have been discovered regarding methods of operation, the use of oils and reagents, and all the other phases of millwork that have a bearing on the success of the process. Routine practice with the process, as carried on to-day, would have been considered impossible four or five years ago. Yet, in spite of these advances on the practical side, few attempts have been made to explain the theoretical side of the process. The results at a flotation plant will often be irregular, and yet the only explanation suggested will be that at such a plant uniformity of results can not always be expected.

Many valuable papers and discussions have been published, but nearly all of these have dealt only with the practical aspects of flotation. The reason for this is not difficult to see. Many of the men who, in their routine work, have had to contend with the troubles that arise at a flotation plant have been interested only in the metallurgical results, and when their problems have been successfully solved have assumed that a change in the ore had been the cause of the troubles and that the use of lime, possibly, has solved their difficulties.

The men in a position to offer a scientific explanation of these troubles and to suggest solutions have been, for the most part, unacquainted with the practical working of the flotation process and hence have been unable to correlate their scientific knowledge with the observed facts.

During five years of flotation work in various parts of the country and as a result of much laboratory experience with ores from widely separated localities many facts have been noted. At first, these various observations were not coordinated, but as more facts were observed at mills in different places, especially the difficulties that

arise and their elimination, the facts gradually were correlated and their relations became more evident.

Recently, it was necessary for the author to take up some work dealing with the chemistry and physics of colloids. As the investigation proceeded, the connection between seemingly disconnected facts and the phenomena of flotation became so remarkable that it seemed that the process could be considered as a specialized phase of the science of colloids.

Many of the relationships mentioned in this paper have been seen, observed, and mentioned by other investigators and are referred to here only to emphasize their importance and not in an attempt by the author to assume credit that belongs to others.

## SULPHIDES NOT WETTED BY WATER.

From the inception of the art of flotation it has been known that the minerals that float are not wetted by water, and that minerals wetted by water—the gangue minerals—are not floated. These facts have been so evident that they have been called fundamentals of the process. Instances in which the valuable minerals could not be floated have been considered freaks and little has been said about them.

If the minerals that float are those not wetted by water a warranted assumption is that the sulphides that do not float have, for some cause, an unusual action toward water. Also, it is reasonable to think that some condition exists that causes the sulphides to be wetted by the water instead of not being wetted, as would be expected. At least, if any sulphides do not float, as some do not, the relation between the water and the mineral is abnormal, and it is reasonable to suppose that this abnormal condition will be evidenced by the sulphide being wetted.

At once the question arises, How can it be that some sulphides will be wetted under one set of conditions and not wetted under other conditions? Such anomalies can exist, and this paper aims to show that it is possible for sulphides, under certain conditions, to be wetted, and how the different factors of flotation can cause the sulphide minerals to be wetted, and to present, incidentally, plausible explanations of this wetting and of some of the other common flotation mysteries that have been so often encountered in practice.

It is understood, of course, that the same conditions that change the action of the water toward the sulphides can also change the character of its action on the gangue minerals.

## COLLOIDS AND ADSORPTION.

Explanation of the phenomena of the wetting and the nonwetting of mineral particles is to be sought in a branch of science that until recently has not been well understood—the chemistry and physics of colloids. All of the different phases of this science are of vital interest to the student of flotation. However the phases most important to the flotation man deal with what is termed adsorption.

Adsorption is a common manifestation of energy but its working is more or less complicated, from the standpoint of the mill operator. The author has endeavored to present the subject in the clearest manner possible, with especial emphasis on the bearing of adsorption on flotation. Of course absolute proof of some of the assumptions made is difficult, if not impossible. However, their practical value should not be lessened on that account. Actual proof of the existence of atoms and molecules was, for a long time, wanting, but no one can doubt the value of the atomic theory as a working basis of chemistry.

### SURFACE TENSION AND SURFACE ENERGY.

In order to approach the subject of adsorption intelligently we must first learn something of surface tension and its relation to colloids. Also, in order to understand surface tension and the factors depending on it, we must investigate surface concentrations, which are closely connected with so-called surface energy.

#### LIQUIDS.

When a liquid is in contact with its own vapor, or with another liquid in which it is not miscible, the surface is in a condition of strain; the surface tension of the liquid being simply a manifestation of this condition of stress. Surface tension is a determinate factor. Clearly, the total amount of energy exerted at the surface of the liquid will be the product of the surface tension (intensity factor) multiplied by the area of the surface over which the surface tension is manifest (capacity factor).[a] Such being the fact, it must follow that the total energy acting on the surface can be reduced by reducing either of these two factors. As regards the mobile liquids, reduction of the surface can easily be accomplished, and the assumption follows that an increase of surface energy comes about when the surface is increased. That a decrease of the surface of the liquid causes a corresponding decrease in the surface energy is illustrated by the fact that the drops of a liquid will tend to assume the shape of spheres, which is, of course, the smallest surface possible for a given volume. This phenomenon is simply the tendency of the surface

[a] Taylor, W. W., The chemistry of colloids, 1915, p. 222.

tension to reduce that surface and to establish an equilibrium with the other forces of the liquid. "As it takes work to produce or enlarge a surface, this is, when formed, the seat of energy, which is measured by the product of surface and surface tension per unit length, and which, of course, tends to become a minimum."[a]

SOLIDS.

The facts just mentioned are well known because the manifestations are easily observed. The problem, when dealing with a solid whose surface can not change, is not so easy to understand, and the conditions must, to a great extent, be proved by analogy. We must ascertain whether the surface energy of a solid is a constant under given conditions, or whether it, also, tends to become a minimum. Of course, a reduction of surface would reduce the surface energy, but such a reduction is clearly impossible with the solid, therefore any change in surface energy must be shown in some other way.

It is known that the surface tension of a liquid is due to molecular concentration in the surface film of the liquid. Therefore, change in the molecular concentration at the surface of a given liquid or a solid may reasonably be assumed to produce a difference in the surface tension and hence in the surface energy of the liquid or solid. Study of the action of the surface of mercury in contact with different gases has shown that a concentration of the gases on the surface of the mercury is accompanied by a reduction in the surface tension of the mercury.[b] Also, it has been proved that compressing a gas or liquid in contact with the surface of a solid will have a similar effect; that is, will cause a reduction in the surface energy of the system.

Therefore it is reasonable to suppose that the same facts will be true of a solid in contact with a gas.

Benson[c] reduced the surface tension of water by means of amyl alcohol and on analyzing the resulting froth found that the proportion of alcohol in the froth was about 5.5 per cent in excess of that in the body of the liquid.

In this connection Hatschek[d] says:

> We have thus some direct evidence to support the view that the changes in concentration, classed together as adsorption, on a surface are due to the tendency of surface energy to attain a minimum value, and that they occur if an increased concentration leads to a reduced surface tension.
>
> Our whole knowledge of the matter is not based exclusively on such reasoning, which, as far as the solid is concerned, rests on the uncertain ground of analogy, but the principal proposition has been proved by thermodynamical methods by Willard Gibbs.

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[a] Hatschek, Emil, An introduction to the physics and chemistry of colloids, 1916, p. 69.
[b] Hatschek, Emil, work quoted, p. 71.
[c] See Taylor, W. W., The chemistry of colloids, 1915, p. 235.
[d] Hatschek, Emil, work cited, pp. 72–73.

Gibbs arrived at the following formula:[a]

$$U=\frac{C}{R}\frac{do}{T}\frac{}{dC}$$

In which $U$=excess of the substance in the surface layer.
$C$=concentration in the bulk of the liquid.
$o$=surface tension.
$R$=gas constant.
$T$=absolute temperature.

From the formula, it can be seen that when a substance is dissolved in a liquid, if the concentration in the surface of the liquid diminishes, then the surface tension increases, but with increased concentration of the dissolved substance in the surface, the surface tension is decreased. Of course, the latter relation is the more common but the former is known and would correspond to "negative adsorption."[b]

### EFFECTS OF SURFACE TENSIONS IN A FLOTATION MIXTURE.

From the preceding discussion it should be evident that surface tension varies under different conditions of heat, pressure, and different concentration of dissolved substances; also that adsorption under different conditions can be either negative or positive. It should be noted that adsorption is only another name for change of surface concentration. If gas concentrates on a surface, the surface adsorbs the gas, a feature of the greatest interest as regards flotation.

In considering flotation, an important fact to be borne in mind is that adsorption is the result partly of surface energy, and consequently of surface tension, and partly of the equilibrium that is established between the surface energies of the water and the solid, and consequently is dependent on both. Adsorption being caused by surface energy acting on both of the substances, is, therefore, the direct result of a condition of equilibrium that will always be established when the surface energies of the substances have become minimum under this set of conditions.

We can now consider minerals that are sulphides. Under normal conditions, that is, with pure water and a particle of bright clean sulphide, equilibrium conditions at the contact surface will be such that the solid will have a negative adsorption toward the water, and a positive adsorption toward air. The reason why the water is not adsorbed is that the mineral adsorbs air more strongly; hence the mineral is not wetted by the water. However, when the amount of surface energy of either the sulphide or the water is changed in any way, evidently the resulting equilibrium would be changed, too. It is evident also that the change in the equilibrium system could be so great

[a] Taylor, W. W., The chemistry of colloids, 1915, p. 223.
[b] Hatschek, Emil, An introduction to the physics and chemistry of colloids, 1916, p. 72.

and of such character that the sulphide would adsorb water in preference to air, that is, would be wetted. This is the condition that the writer has assumed to be true when a sulphide will not float.

When the number of factors that may affect the energy in the surface of any of the substances in a flotation mixture is realized, it is surprising that flotation works so well in practice and is not a more delicate process. The substances that are added to the water to reduce the surface tension and make frothing possible, the foreign elements that may be dissolved in the mill water, and the number of elements in the ore that could act to upset the equilibrium are all potential factors that may change the total energy of either the water, air, sulphide, or gangue surface, and thus cause an equilibrium such that flotation may be bettered or may be made impossible.

The condition of the sulphide itself is an important factor in the total equilibrium of the system, and, hence, can make flotation possible or impossible by disturbing the requisite flotation conditions. The factors that might act to vary the surface energy of the sulphide particles are the sizes of the particles, the character of their surface, the gases present in the pulp that would tend to be adsorbed in preference to oils, and many other conditions that can only be surmised.

## ADSORPTION AND EQUILIBRIUM.

Too much emphasis can not be placed on the fact that adsorption is an equilibrium that can be approached from either side, and is therefore reversible.[a]

It has been shown that if a liquid containing a finely divided suspension is shaken with another liquid that is immiscible with the first, and certain relations between the surface tensions (surface energies) are in equilibrium, then certain results will follow.

In a mixture of water, oil, and solid mineral, if the surface tension between the oil and the solid exceeds the surface tension of the contact between the oil and the liquid, plus that of the contact between the liquid and the solid, the water will have no effect on the solid, which will remain in suspension. But if the tension of the liquid-solid surface is greater than the sum of the tension of the liquid-oil surface plus that of the oil-solid surface, the solid substance will be wetted by the liquid.

If the energy of the liquid-oil contact surface is greater than that of the oil-solid surface plus that of the liquid-solid surface, the solid particles will not be wetted by the water but will collect at the interface of the oil-liquid contact.[b] This is evidently the condition that must hold for satisfactory flotation results.

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[a] Taylor, W. W., The chemistry of colloids, 1915, p. 252.

[b] See Taylor, W. W., The chemistry of colloids, 1915, p. 225; Ralston, O. C., Why do minerals float? Min. and Sci. Press, vol. 3, Oct. 23, 1915, p. 624; Reinders, W., Chem. Weekblad, Bd. 10, 1912, p. 700.

Therefore, flotation results depend on certain relations between the surface energies of the gangue minerals, sulphide particles, oil, and water. Hence, if these relations must exist in order to get flotation of the sulphide particles, then any substance that can vary or change the relation between the surface energies of the factors of flotation will affect the success or failure of the process.

The purpose of the present discussion is to attempt to show that this relationship necessary for successful flotation can be changed by different substances and factors; and therefore, nearly all flotation troubles can be traced to the agencies that can vary the surface energies of the different elements in the flotation pulp and thus change their relationship.

Evidently flotation is a delicate process, extremely susceptible to outside conditions, and practice has shown it to be such.

In studying the effects of adsorption, surface tension, and colloids it will be well to determine the effects of varying the conditions in flotation pulps, and also to attempt to discover the answer to any of the problems that are connected with flotation.

## ACTION OF COLLOIDS.

However, before proceeding to discuss flotation pulps, the colloids and their actions under various conditions will be considered. It has been shown that adsorption depends on the relation of the concentration and surface tensions of the mineral and the liquids; the next step is to determine whether colloids can destroy those conditions of equilibrium necessary for the best flotation results.

As previously stated, the condition of equilibrium between pure water and a clean particle of sulphide is such that the sulphide does not adsorb water and is not wetted. Also this condition has been assumed to produce the best flotation results. From this assumption it follows that in order to get the best results in actual practice, conditions should approach as nearly as possible the equilibrium that exists between pure water and massive sulphides. Such conditions, however, must be established in the presence of the oil added as a frothing agent and of the various compounds in the ore itself that necessarily cause complications; also, at most flotation plants the water used is more or less impure from dissolved salts.

The results of practical flotation work tend to prove that this assumption is more or less correct. As previously shown, the proper equilibrium of the surface energies in a flotation system is the result of several conditions, among them being the character of the sulphide gangue, the salts dissolved in the water, and the physical condition of the oils used. As surface energy is the product of surface tension, the colloids, because of their enormous proportion of surface area, would probably have a greater effect on the surface

equilibrium of the pulp than would any other substance likely to be present.

### PRACTICAL ILLUSTRATION.

Practice in flotation mills has shown that, as regards ores in which the sulphide would not float, the inability to float the sulphide is due to the gangue and not to the sulphide itself. An ore of this sort was the Magna copper ore from Superior, Ariz.[a] In the first attempts to float this ore great difficulty was encountered. On the other hand, ore from the National Copper Co. mine at Mullan, Idaho, could be readily floated. Some of the mineral from the Magna ore, which was hard to treat, was sorted from the gangue and placed in the gangue of the easily floated National ore; the mineral then floated as readily as that in the National ore. The condition of the gangue of the Magna ore was evidently such that the floating of the mineral was retarded, but when the same mineral was mixed with a different gangue the trouble vanished.

### EFFECT OF ENORMOUS SURFACE DEVELOPMENT.

It is reasonable to suppose, from the decided effects of large surface development of the colloids, that colloids in the gangue were the cause of the trouble with the ore mentioned. That colloids would have such an effect is indicated by Taylor,[b] who states that the surface energy of a substance is negligibly small unless the specific surface (area of surface divided by the volume) is at least 10,000. In other words, the surface equilibrium would be only slightly affected by the surfaces of substances present in the pulp, unless the area of surfaces of the material that is entering into the reaction is very large compared with its volume. The enormous proportion of the surface area of colloids is their most important characteristic, therefore, it may be assumed that they would be the most active constituents of the mixture in their effects on surface equilibrium.

### EXAMPLES SHOWING EFFECTS OF COLLOIDAL MATERIAL IN PULP.

Practical flotation tests can be cited to prove that the colloids in the ore were the interfering elements, or factors, that affected the surface equilibrium, so disturbing the relation between the surface tensions of the oil, sulphide, and water that the sulphide mineral adsorbed water; that is, was wetted. Also, the resulting surface-energy relation may possibly have been such that no action between the ore, water, and oil[c] could take place.

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[a] Personal communication to the author by J. M. Callow.
[b] Taylor, W. W., The chemistry of colloids, 1915, p. 223.
[c] Taylor, W. W., work cited, 1915, p. 260.

A noteworthy example that may be mentioned of colloids destroying good flotation conditions is that of the Inspiration Copper Co. The company found, soon after its tests were started, that some of the ore in the deposit was not so amenable to flotation as the larger part of the ore body. The ore that could be floated satisfactorily had for its principal gangue material a hard schist, whereas the ore that would not float well was mostly gangue composed of partly decomposed kaolinized granite.[a]

It was soon found that when the kaolinized (colloidal) material was sent from the mine to be treated directly by flotation, the results were very poor. However, this kaolinized ore could be handled fairly well by mixing it with about 80 per cent of the hard crystalline ore. This mixing did not remedy the trouble entirely, but so masked the effect of the slimed material that the results were comparatively satisfactory.

Also, it was found that when the mine-run ore contained a large proportion of fine material (primary slime) before crushing, the flotation results were poor. Tests of such ore showed that the fine material could be screened out and was very difficult to float, whereas the coarse material that did not pass the screen could be floated in the usual way.[b]

The fact that the trouble did not develop again when the coarse material was ground for flotation may seem to be proof that the size of the particles had nothing to do with the difficulties just mentioned. However, such a conclusion does not follow, because a colloidal slime can not be formed from granular material by grinding. Granular material that has been ground as fine as possible is still granular and is much different from the substances known as true colloids.

### POSSIBLE EXPLANATION.

A plausible explanation for the facts just mentioned, on the basis of the surface-energy equilibriums that have been discussed, is as follows: The equilibrium between the surface energies of the water, ore, and oil in the pulp had been so established that the resultant effect would give good flotation results under normal operating conditions. Of course, the obtaining of good results is proof that the equilibrium established was such that the gangue particles were adsorbing the water positively, while the sulphides were repelling the water and adsorbing the gas and oil in the pulp. As can be seen from the preceding discussion, this effect is caused by the resultant of the systems of forces that are set up at the point of con-

[a] Gahl, Rudolf, History of the flotation process at Inspiration: Trans. Am. Inst. Min. Eng., vol. 55, Sept., 1916, p. 1629.

[b] Gahl, Rudolf, work cited, p. 1653.

tact of all the substances present in the pulp. Evidently this resultant can be easily given an opposite direction by a change in any of the factors involved in surface energy. Colloids, because of their enormous proportion of surface area, can affect this surface equilibrium in two ways. The fact that the specific surface is probably greater than 10,000 would cause the surface energy of the colloids to become very active. This active surface, on suddenly entering the sphere of a nicely balanced equilibrium system, would, it is reasonable to suppose, have a decided tendency to upset the equilibrium between the different factors, with the result that the sulphide would tend to adsorb the water, or possibly a neutral condition would result.

Also, the colloids, owing to their large proportion of active surface area, make active adsorbing agents. There are two substances in the flotation pulp that would be extremely susceptible to adsorption. One is, of course, the substances that are in solution. As has been shown, the concentration of these substances is almost entirely responsible for the value of the surface tension of the solution. The colloids would tend to absorb some of the dissolved material, which would of necessity change its surface concentration and, therefore, the surface tension of the solution. The surface-tension value of the solution is one of the most important factors on which the surface-energy equilibrium of the system depends. Hence, the changing of this one factor alone would tend to upset the existing equilibrium, and thus cause a difference in the adsorption power of the sulphide and the gangue toward the air and the oil.

Furthermore, the colloids actively adsorb other finely divided substances, particularly organic substances, the class in which many flotation oils fall. Hence, the colloids may adsorb sufficient oil to change the concentration of that important factor in the surface-energy system, with the result that a new equilibrium is established which has an entirely different action toward the sulphide particles and the gangue particles.

### CONDITION OF FLOTATION OILS.

One of the important factors that should be taken up at this point is the condition and the actions of the oils that are added to flotation pulps. The soluble portions of the oils are responsible for the frothing of the water. Frothing is, of course, due to the soluble constituents of the oil concentrating on the surface of the water and reducing its surface tension. As has been shown, this reduction of the surface tension is closely related to the frothing propensities of the water. The portion of the oil that is insoluble and is unemulsified in the water, will, owing to the relations of the surface energy of the

system, be adsorbed on the surfaces of the sulphide particles, and not be adsorbed by the gangue particles.

### UNEMULISIFIED OILS.

Before proceeding further, an attempt will be made to show that if the oils in a flotation mixture are emulsified, they will not be active in flotation. That this assumption is true is indicated by several known facts. The knowledge that oils in the bulk or natural state are adsorbed by the sulphides gives one clue. If the oils are emulsified, they are in the condition that corresponds to the colloidal state, and their surface will be extremely active. Also, emulsification again involves a change of surface energy, because the measure of the energy is the product of the surface tension, multiplied by the area of the surface. Hence an increase in the proportion of surface area of the oil will increase its surface energy. If the surface energy of the oil when in the bulky condition will establish such an equilibrium that the sulphide will adsorb the oil, then in all probability when the oil is in the colloidal condition the equilibrium would be such that the oil would not be adsorbed.

Another fact tending to indicate that for good flotation results the oil should not be in the colloidal condition is that emulsions of oil in pure water are extremely unstable, yet pure water gives the best flotation results. Also, oil emulsions in dilute soapy solutions are highly stable and are easily made, yet the trouble caused by soap in flotation pulps is well known.

The use of electrolytes and acids helps flotation, although such substances tend to break up emulsion, and cause the oil to coagulate.[a] The inferences from these facts tend to indicate that the oils in a flotation pulp should not be emulsified.

Adsorption plays an important part in the oil phase of the problem. As has been explained, the surface energy of the system, as shown by adsorption, is a factor of the area of surface exposed. When an oil is emulsified the character of the surface tension and, consequently, the surface energy of the oil are modified. When the oil is in stable emulsion a maximum of surface is exposed, which upsets the surface energy of the oil and hence the equilibrium of the system. As previously stated, oil emulsified with soap is useless for flotation; bulk oil is in the proper condition for being adsorbed by sulphide minerals. Here would seem to be another proof that for good flotation the oils should not be emulsified. When coagulated, the unemulsified oil would be in a condition to modify the liquid. Also, when the oil is in the colloidal (emulsified) condition it has,

[a] Megraw, H. A., The flotation process, 1916, p. 37; Hatschek, Emil, An introduction to the physics and chemistry of colloids, 1916, pp. 41, 43.

owing to the increased surface, a greater tendency to adsorb the modifying elements from the water, and hence a greater chance of upsetting the equilibrium of the surface energies and of carrying these modifying elements out of the zone of action.[a]

It is evident that the actions of the oils in a flotation pulp are complicated, but it is also evident that the surface energy of the oils is a most important factor in establishing the proper equilibrium for successful flotation, and that the surface tensions of the oils, which directly involve their surface energies, are decidedly susceptible to the various conditions that exist in the pulp. It is seen that nearly any substance present in a flotation pulp may affect more or less the surface-energy equilibrium of the oils, water, and minerals.

The question of the oils upsetting the surface-energy equilibrium of the flotation pulp and retarding the flotation of the sulphide minerals will now be considered in more detail.

### SURFACE RELATION OF WATER AND OILS.

As has been shown, the oils have two functions in flotation: To furnish a soluble constituent that will reduce the surface tension and produce froth, and to furnish an insoluble element that will, under the proper conditions, coat the sulphide particles. This brings in another complication, the equilibrium between the surface energy of the water and that of the minerals.

As has been mentioned, water when pure is in the best condition for not being adsorbed by sulphide particles. This can be shown by laying a piece of pure mineral on the surface of pure water; the water will not wet the sulphide. Seemingly, therefore, the equilibrium existing between pure water and the sulphide mineral is close to the correct surface-energy relation to produce good flotation results.

If the assumption that the best condition for flotation is when the mineral is not wetted by the water is true, then in order to get good flotation the relations of the water and the mineral must be changed only in such a way that the resultant of the surface energy of the water and that of the mineral will be the same after the modification as before. In other words, if one of these two phases of the flotation process is changed in amount or character the other must also be so modified that the energies of the surfaces will still bear the same ratio.

The writer can not prove this assumption, but all of the facts seem to indicate that such is the true state of the conditions.

[a] Arndt, Kurt, The colloids in the industrial arts, 1914, p. 43.

## DIFFERENT TYPES OF COLLOIDS.

As suggested previously, the action of the slimes or colloids in the gangue has just as important an effect on flotation conditions as that of the oils themselves.

There are two general types of colloids, reversible and irreversible. The reversible colloids, when they have been coagulated or precipitated, can be easily caused to dissolve again by the solvent from which they were precipitated. The irreversible colloids, once they have been coagulated or precipitated, can not be made to go into solution. Among the reversible colloids are aqueous solutions of gelatin, gum, glue, and tungstic and molybdic acid.[a]

Among the irreversible colloids are stannic acid, ferric oxide, alumina, and arsenic trisulphide. As a general rule the reversible colloids in an aqueous solution "wander" in the direction of the negative pole, whereas the irreversible colloids move in the opposite direction, thus showing an opposite charge.[b]

A fact that is of some interest, as is shown subsequently, is that reversible colloids are almost inactive toward electrolytes, whereas the irreversible colloids are extremely susceptible to them, and a very small addition of an electrolyte will quickly cause coagulation.[c]

Certain organic colloids present in flotation solutions have the property of causing the precipitation of the irreversible colloids in a reversible condition, and of keeping them from being acted on by the electrolytes that may be added to coagulate them. These colloids, because of this action, are called "protective colloids."[d] The action of certain of the protective colloids, such as glue, tannin, and humic acid, should be noted. Seemingly, much of the trouble in flotation plants from the substances just mentioned may be due to their keeping the interfering irreversible colloids, such as ferric hydroxide or alumina, from being precipitated and removed from the surface-energy system, where they tend to upset the equilibrium requisite for satisfactory flotation.

The colloids most likely to be present in flotation pulps are the irreversible ones, and these, as has been stated, are very sensitive to electrolytes. This may explain the beneficial action of copper sulphate, acid, lime, and other electrolytes that are used at different times as an aid to flotation. When a flotation pulp is heated the irreversible colloids are precipitated, and the surface energy of the water is reduced; hence the beneficial effect of heating in flotation work.

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[a] Poschl, V. C., The chemistry of colloids, London, 1910, p. 15.
[b] Rohland, Paul, The colloidal and crystaloidal state of matter, New York, 1914, p. 9.
[c] Poschl, V. C., The chemistry of colloids, London, 1910, p. 16.
[d] Poschl, V. C., place cited.

## BENEFIT FROM REMOVING COLLOIDS.

The preceding discussion has shown that removal of the primary slimes and heating the pulp will, and that the addition of electrolytes usually will, benefit flotation.[a] These three steps all cause flocculation of the slimes in an ore pulp; hence it follows that these slimes, when present, decidedly interfere with flotation, or at least have close relation with the troubles often encountered. It would not be reasonable to believe that all of the conditions could coincide.

Reversible colloids, as has been intimated, are seldom present in a flotation pulp, but when they are present they hinder or may prevent flotation. As previously mentioned, some of the more important reversible colloids are various humus materials, glues, and gelatins. The difficulty that these materials cause in flotation are well known to flotation operators.

Mention should again be made of the protective colloids, in order that the action of this class of materials in a flotation pulp may be emphasized. The flotation process can not be made to work in the presence of humic acid, soaps, sapoins, and the other well-known colloids of the protective type. As suggested, failure when these are present is probably due to the impossibility of removing other colloids in their presence, or to the fact that they are more readily adsorbed than the oils.

### PRACTICAL EXAMPLES.

Numerous instances from flotation practice can be cited that demonstrate the action and effects of colloids, but only three will be mentioned here. In the mill of the Detroit Copper Co. flotation of the primary slimes, which, of course, contain all the colloidal material in the ores, was found nearly impossible. Further tests showed that the hard granular material in the primary slime from the mill could be separated from the slime, and no trouble was experienced in floating this material.

The concentrator at Needles, Cal., treats ores from two different mines. The milling conditions are the same for either ore, yet the two ores act entirely different toward flotation. The ore from one of the mines floats without trouble, whereas that from the other mine is always hard to float. It was found that the difficult ore could be floated by using acid. An unusual feature about using the acid is that the amount needed varies decidedly from time to time.

As regards these two Needles ores, two explanations are possible. One is that the difficult ore contains some agent, such as a small amount of humic matter, that tends to stabilize the oil emulsion, and

[a] Ralston, O. C., and Yundt, L. D., Chemicals used in ore flotation: Met. and Chem. Eng., vol. 17, 1917, p. 543.

give it a colloidal character, thus making it too active for the surface-energy condition needed. The action of the acid would simply be to destroy the emulsifier and cause the oil to become unemulsified and more active toward the sulphides and gangue in the pulp. The other supposition is that the slime in the ore is in such large amount and of such character that the surface-energy equilibrium is changed, the proportionally large area of active surface of the slime making the adsorption conditions such that the sulphide minerals are not affected by the oil but adsorb the water. The acid, in this event, would simply act as an electrolyte and flocculator of the gangue slime, causing it to settle out of the surface-energy system.

In the new flotation plant of the Consolidated Copper Mines Co. at Kimberly, Nev., satisfactory flotation results could not at first be obtained. Laboratory work had shown that the ore was susceptible to flotation, but in the mill the process worked altogether differently. Eventually it was found that the addition of lime was necessary in order to make the ore float well. The mill water contained iron salts in solution, which were precipitated by the lime. When such salts were in solution the bubbles would not pick up the particles of sulphide, but when the salts were precipitated the particles could be floated. It has been shown that salts in solution tend to affect the surface tension, and hence the surface energy of the water. As a result, when the soluble iron was present, the relations of the surface energies of the water, sulphide, and oil were such that the sulphide adsorbed the water instead of the air. Also, the lime may have a flocculating action on the colloids, thus tending to bring about the conditions necessary for good flotation.

Another discovery that was made at the mill of the Inspiration Copper Co. is of interest in this connection. It was found that better flotation results were obtained with pulp from the Marcy ball mills than with the same ore ground in pebble mills. Gahl[a] has offered the explanation that iron from the iron balls used in grinding mills went into solution in the pulp and gave the right flotation conditions. This explanation seems reasonable in view of the facts set forth herein, because the iron may have the effect of rectifying the surface-energy conditions necessary for good results, but another explanation could be offered.

In order to get a clearer insight into the discussion that follows, a series of tests made in one of the well-known gravity concentrators may be mentioned. The company discovered that the pulp from a ball mill gave better results with a gravity concentration machine than when the ore was ground to the same fineness in other types of fine-grinding machines.

[a] Gahl, Rudolf, History of the flotation process at Inspiration: Bull. 117, Trans. Am. Inst. Min. Eng., September, 1916, p. 1656.

As is well known, the pulp that is discharged from the trunnion of a center-discharge mill, such as the Hardinge, is classified before being discharged. Pulp of a certain density can support particles of not more than a certain maximum weight. The sulphides are heavier than the gangue and must be more finely ground in order to be discharged from the mill. In the peripheral-discharge mill, the mineral particles are discharged regardless of their size. Hence, the sulphide particles in the pulp discharged from the Marcy mill at Inspiration were probably larger than those in the pebble-mill discharge.

### EFFECT OF SIZE OF SULPHIDE PARTICLES.

The relation of the size of sulphide particles to flotation results will now be discussed. As previously shown, for good flotation a certain relation must exist between the surface energy of the water, the oils, and the ore. As the surface energy of a substance is dependent on its surface tension and the amount of surface exposed, the amount of surface energy would be different for the same sulphides, depending on whether they had been crushed in a Marcy mill or in a pebble mill. Now, it would seem that the requisite conditions of surface energy for producing the most desirable surface-energy resultant would be when the particles are of the greatest size. This is more evidently true, if one remembers that the best conditions for non-adsorption of the water by the sulphide is to have pure water and massive sulphide.

Another circumstance that has been noticed in practical millwork indicates that there are additional reasons for believing that these assumptions are true. In flotation plants often a screen analysis of the tailing will show that the largest percentage of valuable sulphides not floated is in the extremely fine sizes. At first thought it would appear that the very fine sizes of sulphide particles would float better than the coarser ones. The reason for the condition just mentioned is much like that for the condition previously cited. As the fine-size particles have a surface energy differing from the coarser particles these small sizes tend to cause a resultant condition of surface-energy equilibrium that is not conductive to good flotation. This brings out a fact that may be new. Evidently it is possible, under given conditions, to have all of the ore, and more especially the sulphides, ground too fine for successful flotation.

In this connection it should be said, and by a little thought on the matter from the present viewpoint it should be evident, that under certain conditions the froth, or rather the total surface equilibrium, can be so adjusted that the very fine sulphide particles will be floated, the coarse particles being lost, or can be so changed that the

coarser particles of sulphides will be saved and the very fine particles lost. An example from actual experience is mentioned to illustrate this point.

The Magna Copper Co. is tabling its flotation tailings to recover the mineral that is too coarse to be saved in the flotation machines. Under normal conditions there is a streak of coarse mineral on the table several inches wide. The company had heard that using soda ash or sodium carbonate in the feed helps flotation, and tried this reagent. At once the streak of sulphide on the tailing table was reduced to a fraction of an inch in width. The mill men were certain that an exceptionally high sulphide recovery was being made, but assays proved the mistake of this assumption. The total recovery of copper by flotation and tabling was found to be practically the same, regardless of the quantity of coarse mineral present in the flotation tailings.

There is only one explanation of the results in the example just cited. When the large amount of mineral was seen on the tailing table, a maximum amount of the fine mineral was being recovered by the flotation cells. However, when a large amount of coarse mineral, that could be saved on the table, was floated, more of the fine mineral, which was too fine for the tables to catch, was lost by the flotation cells.

Also, it was noticed that when the coarse mineral was being floated the froth was of different character than when the maximum amount of fine mineral was being floated.

The surface energy of a fine particle of mineral must be different from that of a coarse particle. If conditions were established giving the surface-energy equilibrium required for floating the fine mineral, the coarse mineral would not float and hence would be lost by the flotation machines. On the other hand, when the conditions of equilibrium are right for floating the coarse mineral, the surface energy of the fine particles, resulting from their large proportion of surface area, are such that they would not be held in the froth.

Thus far several points have been discussed regarding adsorption and its relation to flotation, colloids and their possible effects on flotation results, and to some extent the surface-energy theory and the conditions of equilibrium that must exist in order to obtain good flotation results. Ways in which these theories and statements can be usefully applied in actual flotation practice are suggested in the following paragraphs.

### POSSIBLE APPLICATION OF THEORIES IN PRACTICE.

The assumption has been made that when the mineral is not wetted by the water and is wetted by the oil, flotation can be conducted. The simplest example of this is the condition resulting from a con-

tact of pure water, massive sulphide, and bulk oil. Therefore, it would seem that the oil, in order to be most effective, should be in the unemulsified condition, the state approaching nearest to the bulk condition, and, by the same reasoning, pure water should give the best results. Practice has shown that when these conditions are more nearly fulfilled the best flotation results will be obtained.

In other words, impure water may not give the best results unless some means for counteracting the effect of the impurities is provided. The mineral must not be ground too fine, because then the surface becomes so active that trouble will follow. The oil must not be emulsified or ground in the mill for too long a period, because the large proportion of surface area developed will interfere with flotation, and the oil that is in the colloidal state can not be adsorbed in as good a condition for satisfactory flotation as oil that has a decided size of globules.

It has been shown that the presence of colloids in the pulp will tend to cause poor results. If a considerable amount of colloidal material is present, its elimination, or at least the elimination of its ill effects, will be necessary. The best method of elimination is by adding electrolytes that will cause flocculation or precipitation of the colloids present. If this can not be done, there is a possibility of removing them by heating the pulp. When heating fails, washing the ore previous to flotation would remove them. Besides these methods, there is always the possibility of mixing the ore containing the colloids with enough granular ore to cause masking of the harmful effects of the colloids.

When conditions are not favorable for flotation, blaming any trouble on the oils used will usually be of no avail. If the conditions of the ore and the water are such that flotation is feasible, the results obtained with different oils should not vary much. It has been found that when flotation gives certain results with certain oils, any of the other standard oils of the same type will give nearly the same results under similar conditions.

Flotation, as has been shown, is the result of a combination of certain physical conditions, and these conditions may vary between limits, still giving good results, but when the conditions are not right satisfactory flotation can not be had.

Moreover, flotation is a most delicate process because of the many variable factors that can tend to upset the proper conditions of surface equilibrium. When troubles have developed in a flotation plant, the causes of the difficulties will usually be found to be connected with the factors that are known to cause the wrong balance between the surface tensions and surface energies of the oil, the water, and the mineral that is being floated.

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